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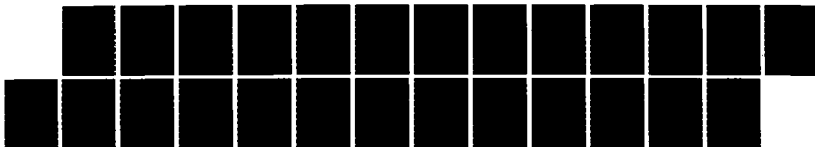
THE MOLECULAR STRUCTURES OF CIS- AND TRANS-1
2-DICHLOROETHENE: A REAL-TIM. (U) ARKANSAS UNIV
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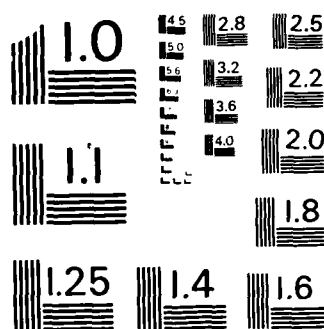
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THE MOLECULAR STRUCTURES OF CIS- AND TRANS-
1,2-DICHLOROETHENE: A REAL-TIME GAS ELECTRON
DIFFRACTION AND AB INITIO STUDY.

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ABSTRACT

The molecular structures of cis- and trans-1,2-dichloroethene were studied in the gas phase by electron diffraction, using our new real-time data acquisition technique. For cis-dichloroethene the structural parameters are (r_g distances (Å) and angles (deg), with 3σ in parentheses): C-Cl:1.717(2); C=C:1.337(4); Cl-C=C:124.0(2); and H-C=C:120.3(3). For trans-dichloroethene: C-Cl:1.725(2); C=C:1.332(8); Cl-C=C:120.8(6); and H-C=C:124.0(3). The experimental work was augmented by ab initio gradient geometry refinements of the two compounds and of cis- and trans-difluoroethene. The 4-21G, 5-31G**, and 3-3-21G basis sets were used in various series of calculations. Without any exception, the calculated structural trends for the cis- and trans-configurations are in excellent agreement with the experiments.



EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

Samples of CDCE and TDCE were obtained commercially (Wiley Organics Comp.) and used without further purification. Electron diffraction data were recorded at room temperature with an acceleration voltage of 40keV, and a scattering distance of approximately 100mm, using our real-time data acquisition system[1,2]. Photodiode array pixel readings were normalized using the ratiometric data analysis procedure developed for real-time data recording[2]. For wavelength calibrations, data were taken for sulfurhexafluoride, SF_6 , and the standard parameters by Bartell and Doun[13] were used. In addition, cursory checks were made against CO_2 , CCl_4 , C_6H_6 , and other standards.

Experimental intensities for the systems studied are shown in Figs.1-3. The corresponding radial distribution (RD) curves are given in Figs 4-6. Individual intensity curves in Figs.1-3 typically range from $s=3$ to about 28\AA^{-1} , and each curve represents the average of 20-30 single data frames[1,2]. For each data frame an integration time of 6 s was chosen to obtain 512 intensity points along the radial line of the diffraction pattern displayed on a phosphor screen. A description of other details of our experimental procedures can be found in refs.1 and 2 and is not repeated here.

The structural parameters reported below were obtained from total intensity curves which are averages of different experiments. In all cases data recorded on different days gave identical results within error limits.

The ab initio gradient geometry refinements were executed with the 4-21G basis[7] on C, F, and H, and the 3-3-21G basis set[8] on chlorine, Cl, with d-functions constructed according to ref.6. In order to test for the basis set dependence of the calculated structural trends, a second series of calculations was executed for CDCE and TDCE with the 5-31G** basis[9] on C and H, combined with 3-3-21G on Cl. All geometries were optimized until the residual forces were insignificant.

RESULTS AND DISCUSSION

The 4-21G structures of CDFE and TDFE are listed and compared with the GED parameters of ref.4 in Table 1. The 4-21G and 5-31G** parameters for CDCE and TDCE are reported in Table 2. The GED results and the correlation matrices of the least squares data refinements are given in Tables 3-5.

Previous tests of our real-time GED data acquisition system have shown[1,2] that intramolecular distances can be determined accurately, but measured amplitudes of vibration are systematically too large compared to literature work. The same characteristic probably applies to the values reported in Table 3. Thus, the C=C bond amplitude in CDCE and TDCE (0.048(10)Å, Table 3) is larger than the approximately 0.040Å to 0.044Å values usually given[14] for this parameter, even though the discrepancy is not too serious. At the same time, our values for $\angle(\text{Cl} \dots \text{Cl})$ (Table 3) are in good agreement with the trends calculated for cis- and trans- $\text{X} \dots \text{X}$ amplitudes in various C_2X_4 systems[14], in which the value for cis is consistently larger than that for trans.

Difluoroethene

The GED parameters of CDFE and TDFE are highly correlated [4]. However, the C-F bond and F-C=C angle (Table 1) are probably sufficiently resolved to consider their differences in the cis- and trans-configurations ($-0.006(4)\text{\AA}$ and $2.7(3)^\circ$, respectively, for CDFE minus TDFE) as credible. The opening of the F-C=C angle in cis as compared to trans is reasonable in view of the C-F dipolar repulsion which exists in the former but not the latter. The calculated differences (-0.004\AA and 3.2° , Table 1) are in good agreement with the experimental values. This shows that even the relatively simple 4-21G basis can reproduce the differences of comparable parameters in systems which are difficult for ab initio calculations due to the presence of fluorine. This lends credence to other trends, for example $+0.001\text{\AA}$ for C=C, and -2.7° for H-C=C (CDFE minus TDFE) which are experimentally not established.

To compare calculated absolute values, rather than relative trends, with experimental ones, the previously established corrections [10-12] for 4-21G structures relative to r_g have to be taken into account. For a C=C double bond in hydrocarbons,

the difference $r_g - r_e(4-21G)$ is $+0.026(3)(2)\text{\AA}[10-12]$. The present results for TDFE and CDFE indicate a smaller value, $+0.015(9)(5)\text{\AA}$ (average for both compounds, Table 1), whereas the corrections for CDCE ($+0.031\text{\AA}$) and TDCE ($+0.028\text{\AA}$) are in the expected range. It is possible that the special properties of F require a different 4-21G correction for C=C bonds conjugated with it.

Dichloroethene

There is good agreement between the present study and ref.3 on the best established GED parameters of CDCE (C-Cl and Cl-C=C, Table 3). Other parameters, however, which are represented by relatively weak signals in the diffraction intensities, such as C=C, C-H, and H-C=C, do not agree within the assigned error limits. Since the accuracy of our procedure in determining molecular structures has been convincingly documented[1,2], and since our GED results (Table 3) are in agreement with the ab initio parameters of CDCE and TDCE (Table 2), whereas the values of ref.3 are not, we have no choice but to consider our model as essentially reliable. The difference, 0.047\AA between the r_g C=C

bond distance of ref.3 and the 4-21G result is unexpectedly large. The same is true for the experimental H-C=C angle of ref.3 ($132(3)^\circ$) which compares to the calculated values of 120.8° (4-21G) and 120.2° (5-31G**). Similarly, the r_g C-H bond distance in ethene is $1.103(2)\text{\AA}$ [15], while the 4-21G r_e value is 1.073\AA [7]. If the same difference, 0.030\AA , is applied to the 4-21G C-H bond of CDCE (Table 2), this yields an expected 1.098\AA for r_g C-H, which is significantly larger than the $1.075(15)\text{\AA}$ reported in ref.3.

In contrast to these discrepancies, our experimental geometries are within the range predicted by the ab initio calculations. Table 2 shows that parameter differences, CDCE minus TDCE, are practically the same in the 4-21G and 5-31G** calculations. Without any exception, these calculated differences also agree with our experimental trends (Table 3).

CONCLUSIONS

The results described above suggest that, compared to TDCE, the C=C bond distance of CDCE is longer by a few thousandths of an Å, the C-Cl bond is shorter by 0.008(3)Å, the Cl-C=C angle is extended by 3.1(6)°, and the H-C=C angle is contracted by 3.7(4)°. Similar trends seem to exist between CDFE and TDFE but with smaller absolute magnitudes.

ACKNOWLEDGEMENT

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REFERENCES

- 1.) J.D. Ewbank, L. Schäfer, D.W. Paul, O.J. Benston and J.C. Lennox, *Rev. Sci. Instr.*, 55 (1984) 1598.
- 2.) J.D. Ewbank, L. Schäfer, D.W. Paul, D.L. Monts and W.L. Faust, *Rev. Sci. Instr.*, in press.
- 3.) M.I. Davis and H.P. Hanson, *J. Phys. Chem.*, 69 (1965) 4091.
- 4.) E.J.M. Van Schaick, F.C. Mijlhoff, G. Renes and H.J. Geise, *J. Mol. Struct.*, 21 (1974) 17.
- 5.) P. Pulay, *Mol. Phys.*, 17 (1969) 197.
- 6.) P. Pulay, *Theor. Chim. Acta*, 50 (1979) 299.
- 7.) P. Pulay, G. Fogarasi, F. Pang and J.E. Boggs, *J. Am. Chem. Soc.*, 101 (1979) 2550.
- 8.) M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro and W.J. Hehre, *J. Am. Chem. Soc.*, 104 (1982) 2797.
- 9.) W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.*, 56 (1972) 2257.
- 10.) V.J. Klimkowski, J.D. Ewbank, C. Van Alsenoy, J.N. Scarsdale and L. Schäfer, *J. Am. Chem. Soc.*, 104 (1982) 1476.
- 11.) L. Schäfer, C. Van Alsenoy and J.N. Scarsdale, *J. Mol. Struct.*, 86 (1982) 349.
- 12.) L. Schäfer, *J. Mol. Struct.*, 100 (1983) 51.
- 13.) L.S. Bartell and S.K. Doun, *J. Mol. Struct.*, 43 (1978) 245.
- 14.) S.J. Cyvin, "Molecular Vibrations and Mean Square Amplitudes", Universitetsforlaget, Oslo, 1968.
- 15.) K. Kuchitsu, *J. Chem. Phys.*, 49 (1968) 4456.

TABLE 1

Comparison of calculated and experimental structural parameters (bond distances in Å, angles in deg) of trans-difluoroethene (TDFE) and cis-difluoroethene (CDFE).

	TDFE ^{a)} (4-21G)	TDFE ^{b)} (ED)	CDFE ^{a)} (4-21G)	CDFE ^{b)} (ED)	DIFF(C-T) ^{c)} (4-21G)	DIFF(C-T) ^{c)} (ED)
C-F	1.3698	1.338(3)	1.3661	1.332(3)	-0.0037	-0.006(4)
C=C	1.3008	1.320(9)	1.3015	1.311(8)	+0.0007	-0.009(12)
C-H	1.0645	1.088(3)	1.0649	1.100(3)	+0.0004	+0.012(4)
F-C-C	119.64	119.8(2)	122.81	122.5(2)	+3.17	+2.7(3)
H-C-C	125.56	125(1)	122.82	127(2)	-2.74	+2.0(2.2)
H-C-F	114.81	--	114.37	--	-0.44	--

- a) 4-21G results, this study. The total 4-21G energies are -172,615.27 kcal/mol (CDFE), and -172,616.72 kcal/mol (TDFE). Largest residual forces in the optimized geometries are <0.001 mdyne.
- b) Electron diffraction r_a structures from ref. 4.
- c) Differences, between the parameters in CDFE minus TDFE, for the calculated (4-21G) and experimental (ED) structures.

TABLE 2

Calculated structural parameters (bond distances in Å, angles in deg) for trans-dichloroethene (TDCE) and cis-dichloroethene (CDCE).

	TDCE ^{a)} (4-21G)	TDCE ^{b)} (5-31G**)	CDCE ^{a)} (4-21G)	CDCE ^{b)} (5-31G**)	DIFF(C-T) ^{c)} (4-21G)	DIFF(C-T) ^{c)} (5-31G**)
C-Cl	1.7388	1.7200	1.7289	1.7121	-0.0099	-0.0079
C=C	1.3053	1.3100	1.3070	1.3117	+0.0017	+0.0017
C-H	1.0668	1.0714	1.0676	1.0718	+0.0008	+0.0004
Cl-C-C	121.61	121.75	125.18	125.43	+3.57	+3.68
H-C-C	123.93	123.55	120.79	120.22	-3.14	-3.33
H-C-Cl	114.46	114.71	114.03	114.35	-0.43	-0.36

a) Ab initio results, this study. The 4-21G basis set (7) was used for H and C; the 3-3-21G basis (8) was used for Cl. The total energies are -622,185.72 kcal/mol (TDCE) and -622,185.36 kcal/mol (CDCE). Largest residual forces in the optimized geometries are <0.001 aJ/Å and <0.001 aJ/rad in bond stretches and angle bends, respectively.

b) Ab initio results, this study. The 5-31G** basis (9) was used on H and C; the 3-3-21G basis (8) was used on Cl. Total energies are -622,282.18 kcal/mol (TDCE) and -622,282.03 kcal/mol (CDCE). Largest residual forces in the optimized geometries are <0.001 aJ/Å and <0.001 aJ/rad for bond stretches and angle bends, respectively.

c) Differences, between the parameters in CDCE minus TDCE, for the 4-21G and 5-31G** structures.

TABLE 3

Structural parameters (bond distances, $r(X-Y)$, and mean amplitudes of vibration, $u(X-Y)$, in Å; and angles, α , in deg) for cis-dichloroethene (CDCE) and trans-dichloroethene (TDCE).

	DH ^{a)}	CDCE ^{b)}	TDCE ^{b)}	DIFF(C-T) ^{c)} (ED)	DIFF(C-T) ^{c)} (5-31G)
$r(C=C)$	1.354(5)	1.337(4)	1.332(8)	+0.005(9)	+0.002
$u(C=C)$	0.038(9)	0.048(7)	0.047(10)	--	--
$r(C-Cl)$	1.718(7)	1.717(2)	1.725(2)	-0.008(3)	-0.008
$u(C-Cl)$	0.048(4)	0.052(3)	0.048(4)	--	--
$r(C-H)$	1.075(15)	1.096(16)	1.092(26)	+0.004(31)	0.0
$u(C-H)$	0.088(16)	0.070(17)	0.077(26)	--	--
$u(Cl \cdots Cl)$	0.117(4)	0.106(5)	0.080(6)	--	--
$u(C \cdots Cl)$	0.062(5)	0.068(3)	0.068(5)	--	--
$\alpha(Cl-C-C)$	123.8(5)	123.95(15)	120.83(58)	+3.12(60)	+3.68
$\alpha(H-C-C)$	132(3)	120.3(24)	124.0(26)	-3.70(35)	-3.33

a) Electron diffraction r_g -values from ref. 3 for CDCE.

b) Electron diffraction r_a -values, this study. Error estimates, in parentheses, are 3σ .

c) Differences between parameters in CDCE minus TDCE for the electron diffraction (ED) and 5-31G** structures (from Table 2).

TABLE 4

Correlation matrix for the least squares electron diffraction data refinement of cis-dichloroethene. The parameter numbering is 1) $r(\text{C}=\text{C})$; 2) $r(\text{C}-\text{Cl})$; 3) $\alpha(\text{Cl}-\text{C}-\text{C})$; 4) $\alpha(\text{H}-\text{C}-\text{C})$; 5) $r(\text{C}-\text{H})$; 6) $\lambda(\text{C}-\text{C})$; 7) $\lambda(\text{C}\cdots\text{Cl})$; 8) $\lambda(\text{C}-\text{Cl})$; 9) $\lambda(\text{C}-\text{H})$; 10) $\lambda(\text{Cl}\cdots\text{Cl})$; and 11) scale factor.

100										
-8	100									
-69	-24	100								
-19	5	8	100							
16	5	-6	-8	100						
-9	-3	5	14	-27	100					
-8	4	2	16	-11	15	100				
0	0	-4	25	-17	40	28	100			
22	0	-16	-3	-1	-10	-2	7	100		
-1	2	-3	18	-6	15	17	30	2	100	
-7	5	-1	36	-23	38	45	71	3	41	100

TABLE 5

Correlation matrix for the least squares electron diffraction data refinement of trans-dichloroethene. Parameter numbering is the same as in Table 4.

100										
21	100									
-82	-50	100								
4	15	-15	100							
22	5	-13	-9	100						
-11	0	7	18	-25	100					
-6	0	3	5	-12	14	100				
-3	3	-1	37	-20	42	23	100			
26	8	-22	4	-1	-3	0	6	100		
-3	2	0	19	-10	13	12	25	0	100	
-7	5	0	50	-26	38	38	72	4	37	100

FIGURE CAPTIONS

Fig.1.

Gas electron diffraction intensities for SF_6 recorded with the real-time data acquisition system of the University of Arkansas. Upper curves are individual experimental molecular intensities, each representing the average of 20-30 single frames; middle curve represents the theoretical molecular intensities $\text{SM}(s)$; lower curves are the differences, experiment minus theory. All curves are plotted on the same scale.

Fig.2.

Real-time gas electron diffraction data for *cis*-1,2-dichloroethene. Plot format as in Fig.1.

Fig.3

Real-time gas electron diffraction data for *trans*-1,2-dichloroethene. Plot format as in Fig.1.

Fig.4.

Theoretical and experimental radial distribution curves for SF_6 . Top curve, experimental; middle curve, theoretical; bottom curve, difference (experiment minus theory). Theoretical data were added to the experimental intensities at small angles for the Fourier transformation, and the damping used was 15pm^2 .

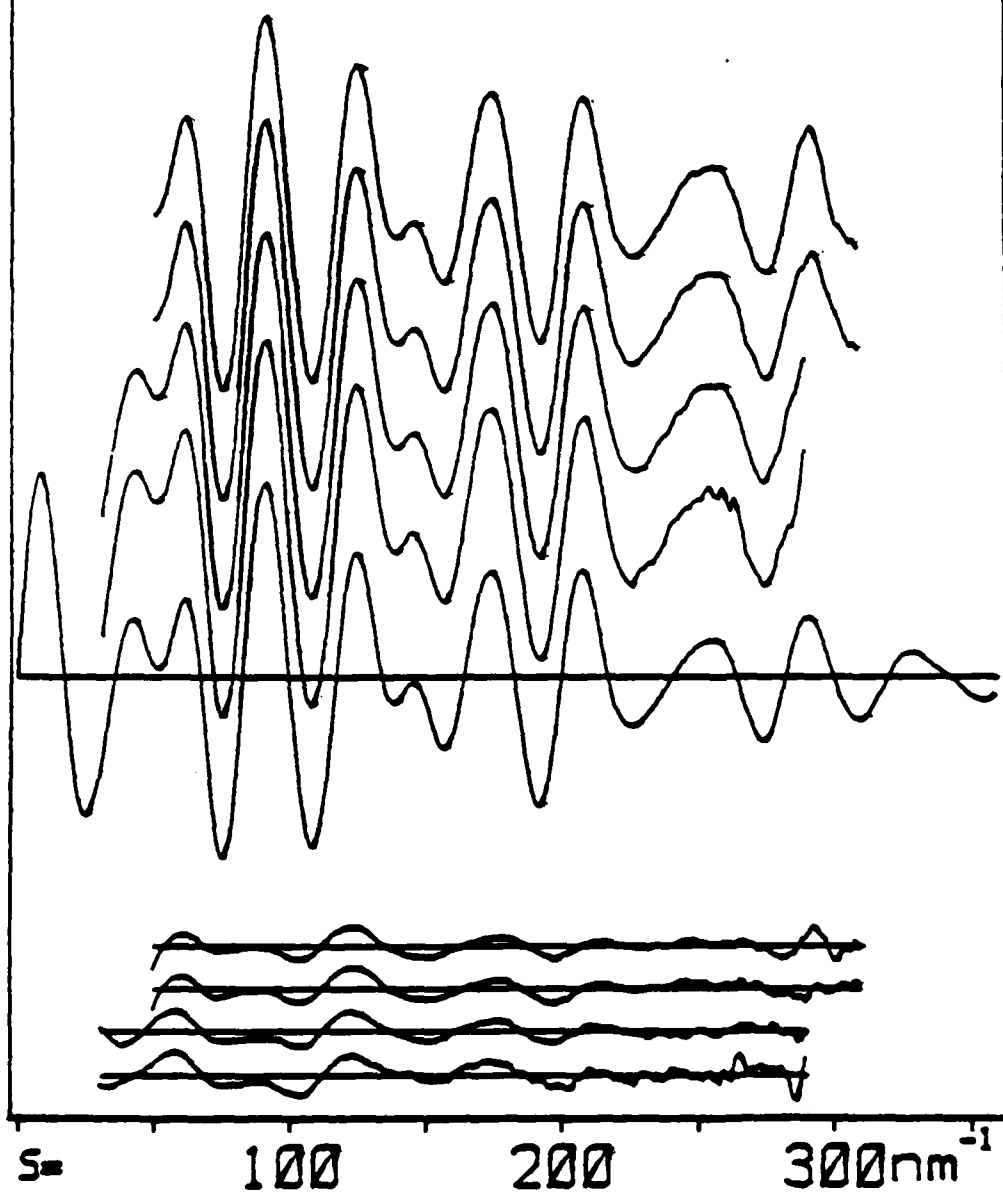
Fig.5.

Theoretical and experimental radial distribution curves for *cis*-1,2-dichloroethene. Plot format as in Fig.4.

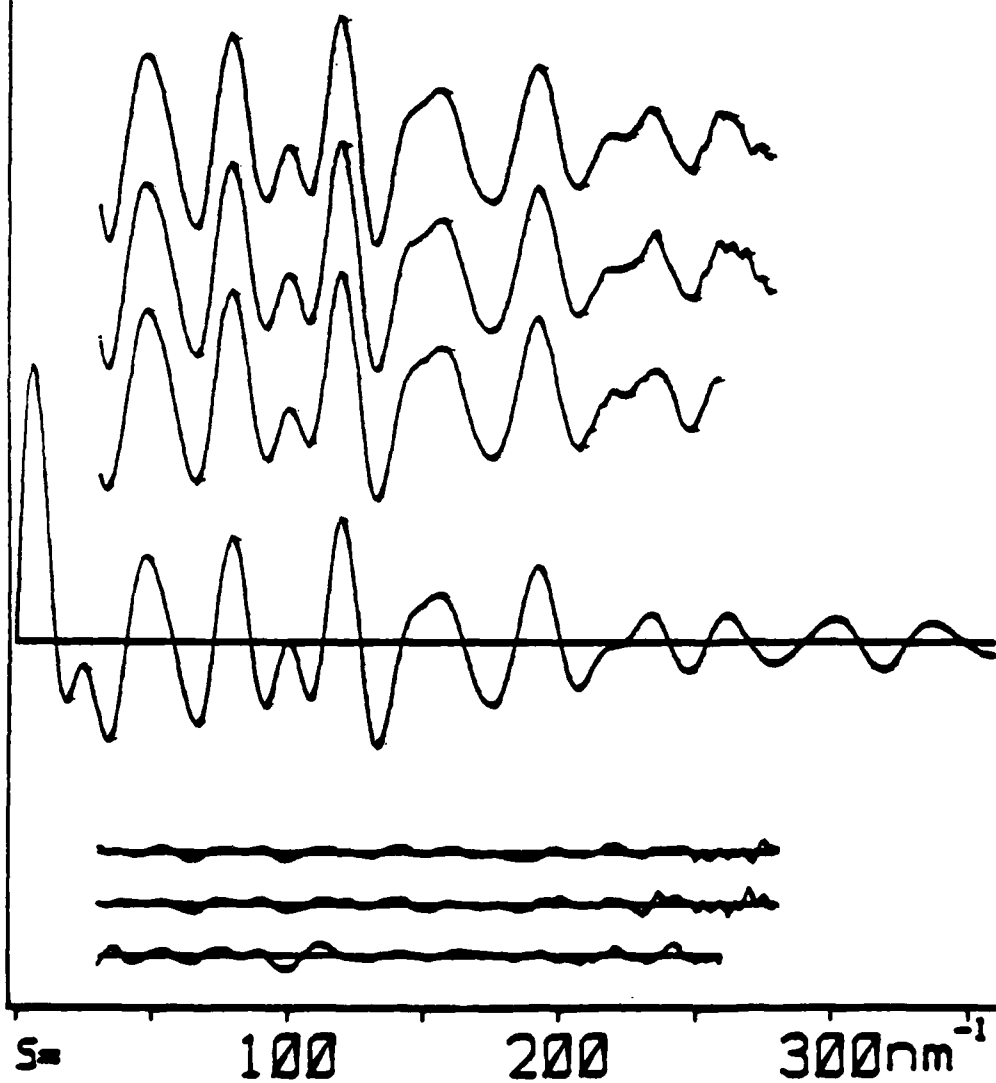
Fig.6.

Theoretical and experimental radial distribution curves for *trans*-1,2-dichloroethene. Plot format as in Fig.4.

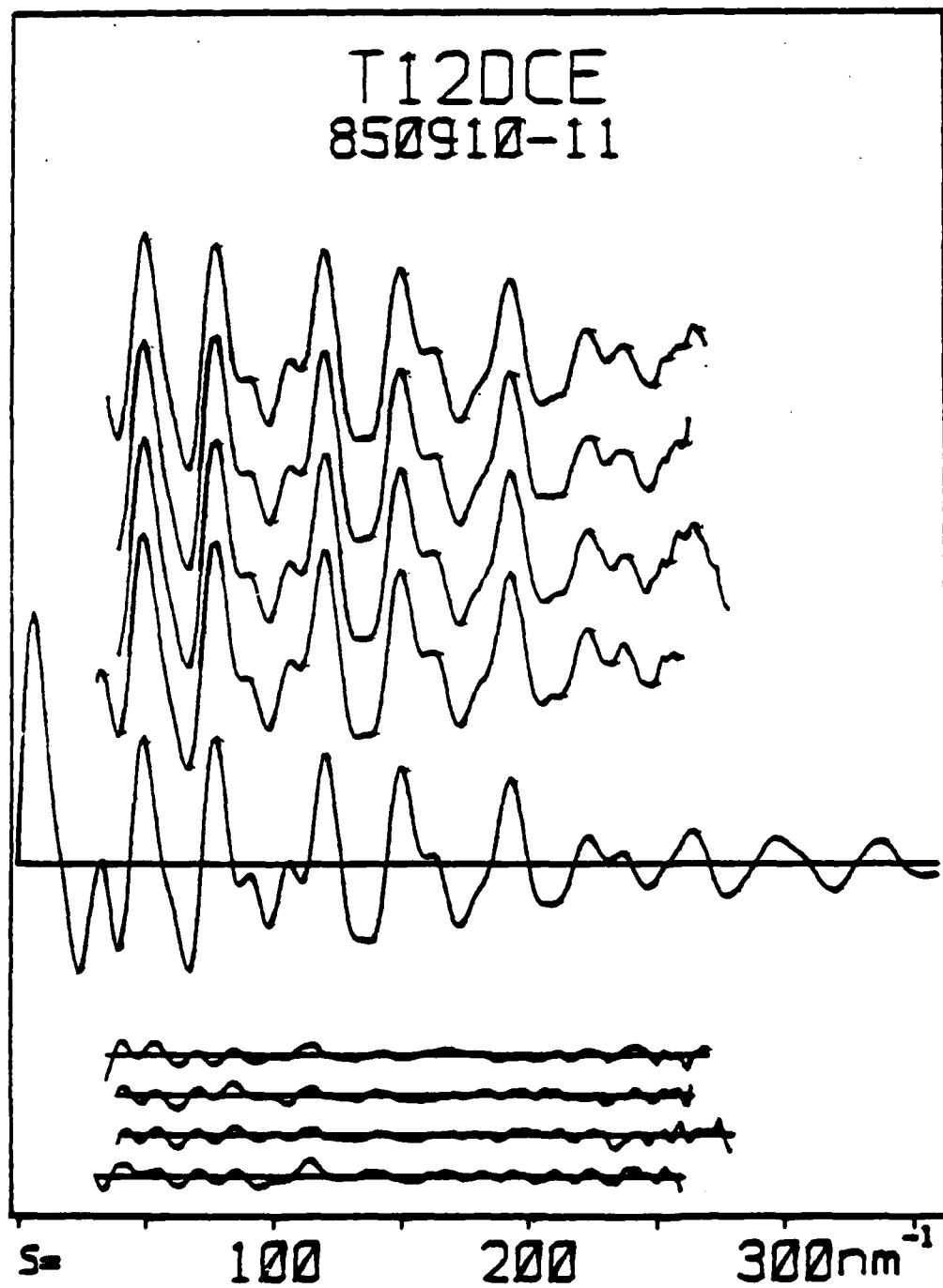
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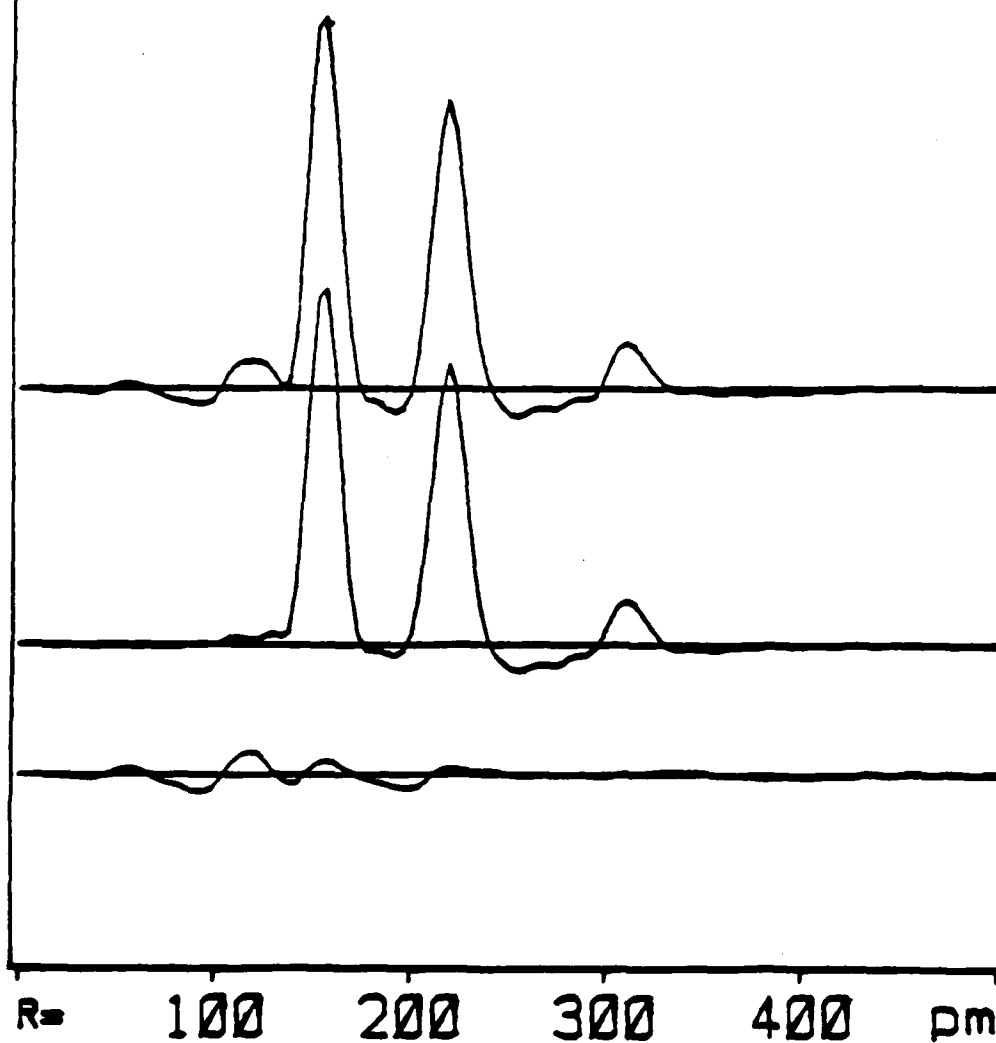
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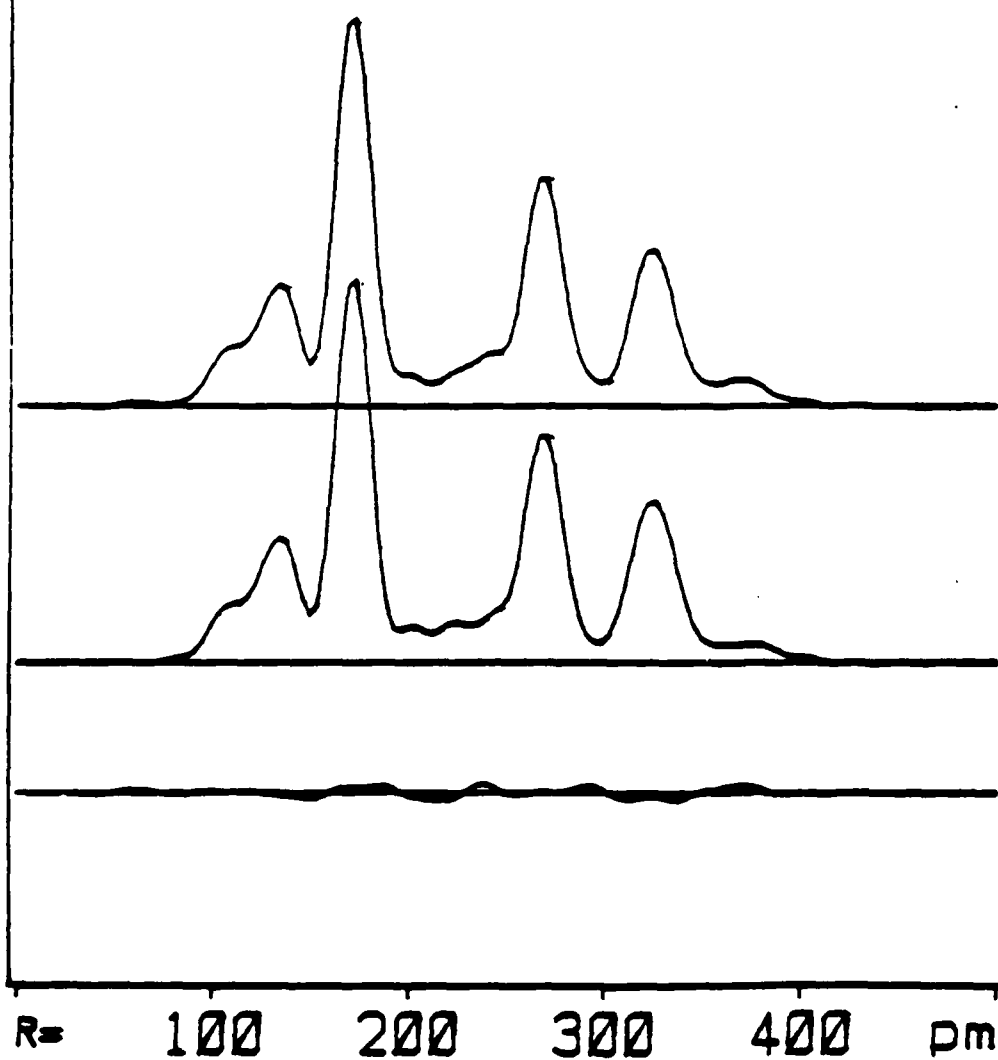
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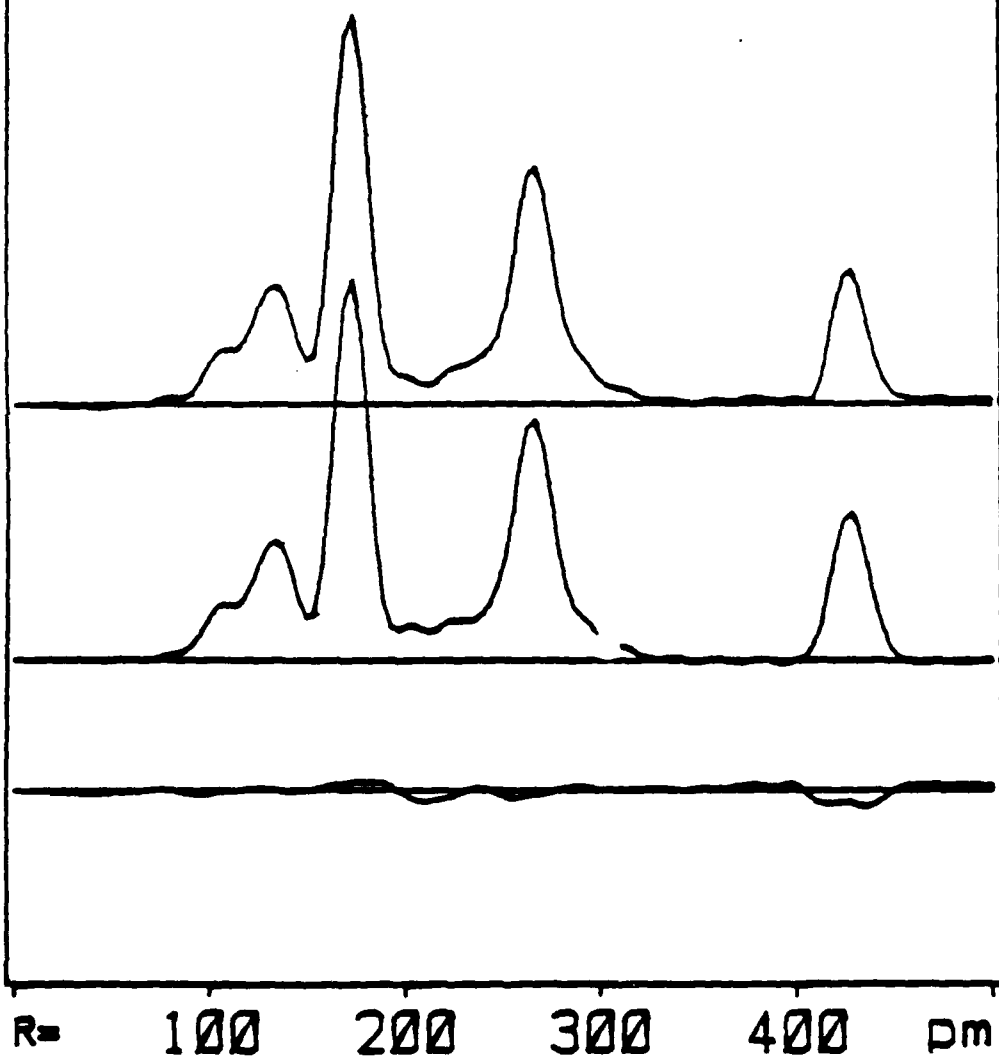
SF6 CALIBRANT
850910-11



C12DCE
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T12DCE
k=.0015 850910-11



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DT/C

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